Applications of metal and non-metal catalysts for the synthesis of oxygen containing five-membered polyheterocycles: a mini review

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Abstract

The investigation of methods for the chemical synthesis is a growing area of interest due to increasing environmental issues. The use of catalysts in organic reactions has gained extensive interest. Metal and non-metal catalysts provided a new improved alternative to traditional methods in modern synthetic chemistry. The aim of present review is to focus on the applications of metals and non-metals for the synthesis of oxygen containing five-membered polyheterocycles.

Keywords Catalysis · Heterocycles · Oxygen

1 Introduction

The heterocyclic compounds are used in chemical, biological, and industrial fields [1–18]. Heterocyclic compounds form the central core of many biologically active natural products and pharmaceutical agents (such anti-viral, anti-inflammatory, anti-bacterial, anti-tumoral, and antioxidant activities agents), and are used in herbicides and corrosion inhibitors. Heterocyclic compounds due to their presence in natural products and biologically active compounds are the most explored compounds [19–51]. They are significant not only for the synthesis of drugs, pharmaceuticals, and pigments, but also for the development of organic functional materials. Many biologically active pharmaceuticals, agrochemicals, modifiers, and additives used in industrial applications like plastics, cosmetics reprography, and information storage are heterocycles in nature [52–73].

Many protocols have been investigated for the synthesis of heterocycles. These protocols for the formation of heterocyclic compounds involve carbon–nitrogen bond-forming reactions such as nucleophilic substitution, reductive amination, or dipolar cycloaddition for ring closure [74–87]. Although various protocols have been developed,

their functional group tolerance and substrate scope is often limited. In recent years, for the synthesis of heterocycles many new protocols have been developed which involved metal and non-metal assisted carbon–nitrogen bond-forming reactions. These reactions tolerated a number of functional groups, occur under mild conditions, and proceed with high stereoselectivity. The utilization of metal and non-metal allows highly convergent multi-component coupling approaches, which form many bonds and/or stereocenters in one-pot protocol [88–90].

Ongoing my interest in the synthesis of five-membered O-heterocycles using silver [66] and the synthesis of seven and higher-membered O-heterocycles using metal and non-metal [67], in this further review we end our overview with the description five-membered O-polyheterocyclic compounds. This review article describes the approaches for the preparation of various five-membered polyheterocyclic compounds with oxygen heteroatom through metal and non-metal assisted reactions. The synthesis of different heterocycles is classified into different categories based on the type of metal and non-metal used.

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2 Metal and non-metal assisted synthesis of five-membered O-polyheterocycles

2.1 Aluminium assisted synthesis

The phenols and phenacyl bromide were reacted via O-alkylation, C–C coupling/cyclization, and dehydration olefination tandem reactions for one-pot synthesis of functionalized benzofurans. The reactions were performed in the presence of alumina supported inorganic bases under solvent-free and microwave irradiation conditions. Ethers were formed as by-products (Scheme 1) [38, 91, 92].

Benzofurans are present in various natural products and possess biological activity and therefore have attracted considerable interest [92–95]. The 2-arylbenzo[*b*]furans were synthesized easily in excellent yields (up to 96%) from α -tosyloxyketones and salicylaldehydes in the presence of potassium fluoride-aluminium oxide (Scheme 2) [96, 97]. The 2-arylbenzo[*b*]furans were prepared under solvent-less conditions from readily available tosyloxyketones and mineral oxides in reactions that were accelerated under MWs.

Scheme 1 Synthesis of 3-phenylbenzofuran

Scheme 2 Synthesis of 2-arylbenzo[*b*]furans

Scheme 3 Synthesis of 3-allylisobenzofuran-1(3*H*)-one

2.2 Bismuth assisted synthesis

The 3-allylphthalide was formed in high yields by Barbier-type reaction of allyl bromide and phthalaldehydic acid with bismuth chloride/magnesium [98] or bismuth chloride/zinc [99] (Scheme 3) [100]. Various pharmaceutically interesting phthalides are found, for example in plants from the Apiaceae family [101].

2.3 Cesium assisted synthesis

Ugi four-component reaction is one of the powerful routes to access structural complexity [102]. Moreover, the Ugi four-component reaction adducts were converted into several cyclic scaffolds via post-Ugi conversions which allowed a facile access to various biologically relevant heterocyclic compounds. Among them, benzofuran structural functionality is present in many pharmacologically active natural products. The benzofurans were synthesized via Rap–Stoermer reaction of the linear dipeptide-like Ugi-4CR adducts under microwaves [103]. The aniline was reacted with salicylaldehydes in the presence of cesium carbonate

under controlled microwave heating in acetonitrile for 15–30 min at 80–140 °C to directly provide benzofurans in 43–90% yields. With benzofurans in hand, two different heterocyclic compounds (2-oxindoles and 5,6-dihydro-phenanthridines) were easily prepared by intramolecular direct arylation and intramolecular *N*-arylation processes in the presence of Pd catalyst (Scheme 4) [38, 104–107].

2.4 Chromium assisted synthesis

The carbonyl-ene-yne was reacted with styrene in catalytic amount of $\text{Cr}(\text{CO})_5(\text{THF})$ to produce (2-furyl)cyclopropane in 85% yield [108]. Complexes of late transition metals, like rhodium, ruthenium, palladium, iridium, and platinum, also catalyzed the cyclopropanation involving (2-furyl) carbene intermediates. The highest catalytic activity was shown by complex rhodium acetate in the cyclopropanation reaction. Electron-rich alkenes like ketene diethyl acetal and *tert*-butyl vinyl ether acted as good acceptors of carbene intermediates to afford the excellent yields of

cyclopropanated products. The complex rhodium acetate served as an effective catalyst for cyclopropanation with an alkyl ketone to afford the cyclopropanated product in lower yield under other transition metal catalysis. Miki and co-workers synthesized (2-furyl)-cyclopropanes by transition-metal-catalyzed cyclopropanation of alkenes with 1-benzoyl *cis*-1-en-3-yne (Scheme 5) [109, 110]. Many transition-metal complexes, like $\text{Mo}(\text{CO})_5(\text{THF})$, $\text{Cr}(\text{CO})_5(\text{THF})$, $[\text{RuCl}_2(\text{CO})_3]_2$, $\text{W}(\text{CO})_5(\text{THF})$, palladium chloride, $[\text{RhCl}(\text{cod})]_2$, and platinum chloride, acted as catalysts for this transformation [78–87, 111].

2.5 Gold assisted synthesis

He and co-workers [112] synthesized benzofurans from aryl allyl ethers via Ph_3PAuOTf -catalyzed Claisen rearrangement. This was followed by a tandem phenol addition (Scheme 6) [113, 114].

Pale et al. [115] reported a reaction of unactivated ω -acetylenic acids for the construction of different

Scheme 4 Synthesis of benzofurans

Scheme 5 Synthesis of (2-furyl)cyclopropane

Scheme 6 Synthesis of 2-methyl-2,3-dihydrobenzofuran

Scheme 7 Synthesis of (Z)-3-ethylideneisobenzofuran-1(3H)-one and 3-methyl-1H-isochromen-1-one

Scheme 8 Synthesis of 1,3-dihydroisobenzofuran-5-ol and 1,3-dihydroisobenzofuran-4-ol

ring-sized lactones. A straightforward trick was applied to boost the nucleophilicity of carboxylic group: a catalytic amount of potassium carbonate to produce the carboxylate anion. The limitations and regioselectivity of the reaction was examined by choosing gold(I) chloride catalyzed cycloisomerization of γ - and δ -acetylenic acids [116]. Both the *exo*- and *endo*-derivatives were obtained by intramolecular cyclization of γ - or δ -acetylenic acids. Uchiyama and co-workers [117] developed an acid-catalyzed regiocontrolled intramolecular 6-*endo-dig* cyclization of γ -acetylenic acids. On the other hand, the *exo-dig* cyclization occurred predominately in gold-catalyzed cycloisomerization reaction to provide the lactones

as a single stereoisomer *Z* and as the major products (Scheme 7) [118].

The phenols were synthesized by the reaction of 5-(2-furyl)-1-alkynes in the presence of AuCl_3 catalyst (Scheme 8) [119, 120]. The substrates such as 5-(2-furyl)-1-alkynes substituted at C-5 of the furan were cyclized to provide the phenols. The reaction occurred via an intramolecular [4 + 2] cycloaddition which was promoted by the η^2 -coordination of gold(III) chloride to the alkyne [78–87, 121].

The *tert*-butyl(dimethyl)silyl protecting group was changed to a benzyl group which afforded high yields without loss in reactivity after using first time. The

catalyst system was so stable that high reactivities and yields were reported even after air exposure for several days. The gold-catalyzed cycloisomerization with gold(III) bromide/[BMIM][PF₆] system was also used for exocyclic α -hydroxyallene (Scheme 9). This substrate was difficult to cyclize and provided the expected bicyclic 2,5-dihydrofuran [122–124].

Before 2008, it was found that cationic [(NHC)Au] compounds catalyzed various “classical” enyne skeletal rearrangements [121, 125–131] which involved the synthesis of an auracarbene [132–141]. Recently, Zhang et al. [142] changed the olefin of an enyne with a carbonyl group and explored the benefit of reactivity of ynones with gold to produce interesting dipoles. This method allowed the synthesis of furan-fused polycyclic compounds (Scheme 10) [143].

Larock [144] and others [145] synthesized substituted furans from 2-(1-alkynyl)-2-alken-1-ones in the presence of transition metal catalyst [146–153]. The reaction occurred through the formation of an oxonium ion intermediate. During the development of a diversity-oriented tandem reactions for the preparation of heterocycles [154–161], authors reported a protocol for the construction of 3(2*H*)-furanones from 2-alkynyl-2-hydroxy carbonyl compounds, which occurred via cationic cyclization (Scheme 11). The

electrophilicity for an intramolecular nucleophilic attack was enhanced upon the coordination of the triple bond of propargylic alcohol to a suitable transition-metal catalyst. The oxonium ion intermediate triggered an irreversible 1,2-shift analogous to a formal α -ketol rearrangement, [162–166] and subsequently protonation of the carbon-transition-metal bond occurred to regenerate the catalyst and provide the 3(2*H*)-furanones. The primary amines were used *in situ* condensation step to expand the diversity of structures obtained from propargylic alcohol, and finally a 1,2-migration occurred to the adjacent iminium ion to afford 3-pyrrolones. The onium ion rearrangements were not utilized to terminate cationic cyclizations, while the related pinacol rearrangements were used to demonstrate the powerful protocol for designing cascade reactions [167–171].

This easy three step sequence was reported for the construction of aurone skeletons [172], natural flavonoids. Aurones possess many biological properties [173–177], and due to this many groups were interested in the development of convenient synthetic pathways [178–184]. The best results were reported with gold-catalyzed oxycyclization and have advantages such as excellent selectivities, milder reaction conditions, and avoided the formation of byproducts like flavones

Scheme 9 Synthesis of bicyclic 2,5-dihydrofuran

Scheme 10 Synthesis of 1,4,4-trimethyl-3-phenyl-4,5,6,7-tetrahydroisobenzofuran

Scheme 11 Synthesis of 4-methoxy-2-phenyl-4,5,6,7-tetrahydrobenzofuran

(Scheme 12) [185]. In this case, complete regioselectivity and high yields were obtained [186].

The base-assisted domino nucleophilic addition/annulation of simple *ortho*-alkynylbenzaldehydes was explored in-depth in the presence of alcohols (Scheme 13). Authors concentrated to rationalize the relationship between the nature of the cyclization mode and the substitution on the alkynyl terminus and on the selective preparation of the isobenzofuran framework [187, 188].

2.6 Gold and silver assisted synthesis

In carbonyl addition to alkynes, Hashmi and co-workers [189] used Boc-protected alkynylamines for similar cyclizations to afford oxazolinones, although the scope was limited to silyl-protected or terminal alkynes. Shin [190] noted that 3-*O*-Boc-1,5-enynes underwent highly diastereoselective cyclizations. *t*-Bu group acted as a leaving group, and this reaction led to highly substituted cyclohexene-fused carbonates (Scheme 14). An efficient tandem cyclization of *tert*-butyl carbonate derivatives of hex-1-en-5-yn-3-ol occurred in the presence of gold(I) catalyst where nucleophilic participation of the *O*-Boc

Scheme 12 Synthesis of (*Z*)-2-benzylidenebenzofuran-3(2*H*)-one

Scheme 13 Synthesis of 1-methoxy-3-methyl-1*H*-isochromene and isobenzofuran

Scheme 14 Synthesis of (3*aS*,4*R*,7*R*,7*aR*)-3*a*,4,5,7-tetramethyl-3*a*,4,7,7*a*-tetrahydrobenzo[*d*] [1, 3] dioxol-2-one

group appeared to intercept a carbocationic (or cyclopropyl carbene) Au intermediate [191]. The reaction led to densely functionalized cyclohexene-3,4-diol derivatives where 1,2,3- or 1,2-stereocenters were controlled in a highly diastereoselective manner [114, 118].

The gold-catalyzed double intramolecular hydroalkoxylation was reported, for the construction of bis-benzannulated spiroketal core of natural bioactive rubromycins [192, 193], by Zhou et al. [194] (Scheme 15).

Wang and co-workers [195] synthesized polysubstituted C-vinyl butyrolactones via a gold-catalyzed highly diastereoselective cyclization of malonate substituted allylic acetates. The *syn*-4-acetoxycyclohexenyl malonate was treated with AuPPh₃Cl/AgSbF₆ at 70 °C in 1,2-dichloroethylene for 3 h for the synthesis of 3,4-*anti*-4,5-*syn*-3-methoxycarbonyltetrahydrobenzobutyrolactone in 80% yield [194, 196, 197] (Scheme 16).

Liu and co-workers [198] synthesized 3-carbonylated benzofuran derivatives by Au(III)-catalyzed tandem rearrangement/cyclization reaction of β -phenoxyimino ketone. The β -phenoxyimino ketone was prepared *in situ* from *O*-arylhydroxylamines and 1,3-dicarbonyl compounds (Scheme 17) [194].

Ketals are crucial targets and important key structures in organic synthesis [199–201]. Fused, bicyclic and spiroketals are recurring moieties in natural compounds, and their synthesis is a key step in many total preparations. Specially, spiroketals are present in various biomedically relevant non-natural and natural systems [202–205]. Many protocols were developed for the preparation of spiroketals, the most common was the cyclocondensation of ketone diols [206, 207]. Nevertheless, cycloisomerization on alkynediols in the presence of gold catalyst has emerged as an efficient protocol to build complex ketal systems in just one step, providing specific benefits. For example, cycloisomerization of alkynediols with Au catalyst was more atom economical, exothermic, and more compatible than ketones under various reaction conditions. Recently, many groups have introduced the present strategy for the preparation of many natural compounds and derivatives [208–211]. Li and co-workers [212] synthesized bisbenzannulated spiroketal core of rubromycins. These natural occurring structures possess many biological properties like inhibition of the reverse transcriptase of HIV I, inhibition of DNA polymerase, or inhibition of DNA helicase [213–216]. Scheme 18 depicts the basic structure moiety shared by natural isolated compounds such

Scheme 15 Synthesis of bis-benzannulated spiroketal core of natural bioactive rubromycins

Scheme 16 Synthesis of 3,4-*anti*-4,5-*syn*-3-methoxycarbonyltetrahydrobenzobutyrolactone

Scheme 17 Synthesis of 3-carbonylated benzofuran

Scheme 18 Synthesis of benzofurans

Scheme 19 Synthesis of 2-aryl-3-aminobenzofuran

as purpuromycin, γ -rubromycin, or heliquinomycin. Easily synthesized alkynediols underwent gold catalyzed cycloisomerization to afford moderate yields of spiroketals along with benzofuran in notable amounts [186].

2.7 Indium assisted synthesis

Chen et al. [217, 218] reported InCl_3 catalyzed synthetic protocol for the synthesis of 2-aryl-3-aminobenzofuran derivatives by the reaction of phenols, arylglyoxal monohydrates, and *p*-toluenesulfonamide (Scheme 19). Some of the benefits are: (1) InCl_3 is easily available and economical catalyst, the formation of by-products α -diketones was inhibited unlike in other Lewis acid catalyzed three-component reactions; (2) this reaction is important for the synthesis of compound libraries in combinatorial chemistry as structurally diverse benzofuran derivatives were prepared from various arylglyoxal monohydrates and phenols bearing different functional groups [219].

2.8 Iodine assisted synthesis

Tripathi et al. [220] reported a 5-*exo-trig* cyclization of *o*-allyl phenols for the preparation of dihydro-benzofurans

Scheme 20 Synthesis of dihydro-benzofurans

in water (Scheme 20). Products were obtained after the formation of iodoiranium intermediate followed by 5-*exo-trig* cyclization. This method worked for phenols which contain electron withdrawing as well as donating groups. The formed dihydrofurans were dehydrohalogenated in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene to give benzofurans [221].

Kobayashi et al. [222] reported a 5-*exo-trig* cyclization of *o*-vinylbenzyl alcohols for the synthesis of 1,3-dihydroisobenzofurans. The *o*-vinylbenzyl alcohols were prepared by the reaction of 2-vinyl phenyl lithium and carbonyl compounds (Scheme 21). The yield decreased when an electron donating group was present on the aryl ring. The

obtained (1-iodomethyl)-1,3-dihydroisobenzofurans were then either alkylated with sodium thiolate or reduced with tributyltinhydride [221].

Larock et al. [223] reported 6-*endo-dig* and 5-*exo-dig* cyclization for the synthesis of five- and six-membered iodo heterocycle respectively from *o*-alkynylbenzyl alcohols (Scheme 22). The iodoirenium intermediate was formed when iodine coordinated with the carbon-carbon triple bond. Nucleophilic attack of hydroxyl group occurred by 5-*exo-dig* and 6-*endo-dig* cyclization to afford the intermediate [221].

Iminoethers act as important building blocks which were hydrolyzed under mild reaction conditions. Dienamides were transformed conveniently to iminoethers [224]. For example, the bromosubstituted iminoether was formed in 53% yield when the starting compound was reacted with NBS. Furthermore, higher yields of halo substituted iminoether were obtained when starting

compound was treated with I_2 in *N*-bromosuccinimide. The iodo-substituted iminoether was formed in 90% yield [225, 226] (Scheme 23).

The reaction conditions were modified for hetero-1,3-diyne in order to achieve single or double cyclization (Scheme 24). Thus, unsymmetrical as well as symmetrical, bisheterocyclic units with dihalide moiety were easily accessible employing this protocol. Similar dihalo compounds were utilized as substrates for the preparation of more complex fused heterocyclic compounds which possess potential applications as organic field effect transistors (OFETs) [223, 227, 228].

The 2-arylbenzofurans were formed by a convenient metal-free cyclization of *ortho*-hydroxystilbenes in the presence of hypervalent iodine reagents. Desired products were obtained in good yields employing stoichiometric (diacetoxyiodo)benzene in CH_3CN [229] (Scheme 25).

Scheme 21 Synthesis of 1,3-dihydroisobenzofurans

Scheme 22 Synthesis of 1,1-diethyl-4-iodo-7-nitro-3-phenyl-1*H*-isochromene and (*Z*)-1,1-diethyl-3-(iodo(phenyl)methylene)-6-nitro-1,3-dihydroisobenzofuran

Scheme 23 Synthesis of (*E*)-tetraethyl 2-(benzylimino)-7a-(iodomethyl)-3-methyl-7,7a-dihydrobenzofuran-5,5,6,6(2*H*,4*H*)-tetracarboxylate

2.9 Iron assisted synthesis

The coupling reactions with both non-substituted and *N*-benzylsubstituted 2-iodoaniline as the arylating agents were very clean, and selectively afforded the high yields of Sonogashira coupling products, without any side reactions on the amine functionality. On the other hand, when 2-iodophenol was utilized, benzofurans were formed from domino Sonogashira coupling reactions followed by intramolecular hydroalkoxylations in moderate yields together with recovered aryl acetylenes (Scheme 26). Although the utilization of iron catalysts and Ag additives for the addition of a hydroxy functionality to olefins is known [230], to the best of knowledge these were the first noted exclusive iron-catalyzed hydroalkoxylations of alkynes. Further experiments, to expand the substrate scope and to improve the conversions of this unprecedented transformation, are currently under study.

2.10 Lithium assisted synthesis

Acetylene-based compounds are very important in synthetic chemistry. The alkynes underwent [2 + 2 + 2] cyclotrimerization to provide hexasubstituted benzenes in one step [231–235]. They acted as useful intermediates for the preparation of biologically active and naturally occurring compounds like dehydrotremetone [236], lunularic acid [237], and cicerfuran [238]. The acetylene functionality was also used in compounds which possess interesting optical, electronic, and other materials-based properties [239–244]. Several acetylenic-based compounds were reported for use as nonlinear optics and molecular wires [245, 246] (Scheme 27).

The thianthrene was submitted to reaction as shown in Scheme 28, after reacting with a first carbonyl compound, the lithiation was continued at –90 to –78 °C with second carbonyl compound, a second carbon-sulfur cleavage occurred to provide organolithium intermediate which was reacted with the electrophile present in the reaction medium to give diols [247–249]. These diols were cyclized with 85% phosphoric acid

Scheme 24 Synthesis of 4-iodo-3-(3-iodobenzofuran-2-yl)-1*H*-isochromen-1-one

Scheme 25 Synthesis of 2-arylbenzofurans

Scheme 26 Synthesis of 2-phenylbenzofuran

Scheme 27 Synthesis of 2-(prop-1-en-2-yl)benzofuran-5-carbaldehyde

Scheme 28 Synthesis of 1,1-dimethyl-3-phenyl-1,3-dihydroisobenzofuran

Scheme 29 Synthesis of 2,2-dimethyl-2,3-dihydrobenzofuran

Scheme 30 Synthesis of 3-aryl-benzo[b]furans

under reflux in toluene to synthesize the substituted phthalans [250].

The 1,3-dioxanes were reacted with catalytic amount of 4,4'-di-*tert*-butylbiphenyl and lithium at -78°C in tetrahydrofuran to produce an intermediate, which underwent intramolecular nucleophilic substitution to form compounds (Scheme 29) [251]. These hydroxy phenols were cyclized under acidic conditions to give benzofused heterocyclic compounds [250].

2.11 Palladium assisted synthesis

Yang et al. [252] reported that cationic Pd complexes showed high reactivity toward coordination of alkynes or alkenes for efficient carbonylation processes. These cationic complexes were easily synthesized *in situ* by reaction of Ag salts of ClO_4^- , BF_4^- , and BAR_4^- with organopalladium halides in the presence of chelating diamine (diimine) ligands or tertiary phosphine ligands. The starting

Scheme 31 Synthesis of (*Z*)-1-benzylidene-1,3-dihydroisobenzofuran

Scheme 32 Synthesis of 2-substituted benzofurans

Scheme 33 Synthesis of substituted benzofurans

Scheme 34 Synthesis of substituted benzofurans

substrate was not converted into 3-aryl-benzo[*b*]furans in the absence of Ag-salt, only phenol ester was obtained (Scheme 30). An complex intermediate was produced from organopalladium iodide. This complex bear a cationic metal center with Lewis acid character and coordinated strongly with unsaturated triple bond [253].

The tandem process shown in Scheme 31 comprised an intermolecular Sonogashira coupling and an intramolecular cyclic hydroalkoxylation [254, 255]. The C–C bond formation occurred in the absence of additives other than the base. The cyclization reaction was highly selective towards five-membered ring and *Z* isomer. Neither the six-membered ring nor the *E* isomer were formed. The final product was obtained from *o*-iodobenzyl alcohol in full conversions (95% yield) in less than 1 h. The higher catalytic activity was observed for complex as compared to the ubiquitous palladium acetate and $\text{PdCl}_2(\text{PPh}_3)_3$ under same reaction conditions.

Fancelli and co-workers [256] reported a Cu/Pd heteroannulation of terminal acetylenes with resin bound aryl iodides to synthesize 2-substituted benzofurans (Scheme 32) [37].

Kabalka et al. [257] reported a microwave-assisted solvent-free Sonogashira coupling of iodophenol with terminal alkynes on KF doped alumina for the synthesis of benzofurans (Scheme 33). The *o*-ethynylphenols were reacted with aryl or alkyl iodides to afford the moderate yields of substituted benzofurans (Scheme 34) [38].

The racemic propargylglycine derivative was reacted with 2-iodophenol under Sonogashira coupling conditions to provide the appropriate precursor in order to investigate the possible synthesis of a 2-substituted benzo[*b*]furan via Ag- or palladium-catalyzed intramolecular reaction (Scheme 35). The expected precursor was formed in 64% yield under these conditions, but in addition 16% yield of the eventually desired tryptophan analogue

Scheme 35 Synthesis of 2-substituted benzo[*b*]furan

was obtained. The obtained mixture without separation was subjected to AgOTf in refluxing CH₃CN to examine whether this catalyst would effect the cyclization of phenol into benzofuran. Unfortunately, however, no increase in the conversion of phenol into benzofuran was reported when the mixture was refluxed in the presence of AgOTf for more than 20 h. This was due to the lower nucleophilicity of the phenol in comparison to the anilines. Therefore, diethylamine (1 eq.) was added to the reaction mixture to examine if this would facilitate the synthesis of benzofuran. Indeed, phenol was converted into benzofuran rapidly upon the addition of diethylamine, however, the reaction led to partial decomposition of the remaining phenol and also did not go to completion. Thus, a mixture of phenol and benzofuran was formed in a combined yield of 71% and an improved ratio in favor of benzofuran when acetylene was subjected to modified conditions [258].

For this tandem cross-coupling cyclization reaction, [259–261] authors transformed enantiomerically pure propargylglycine into propargylglycine derivative by esterification utilizing thionyl chloride in methanol and subjected it to *p*-toluenesulfonyl chloride and pyridine in dichloromethane. Subsequently, acetylene was reacted with 2-iodophenol under modified Sonogashira conditions to

provide the intermediate phenol, which was completely consumed after 4 h to afford the enantiopure tryptophan analogue in 74% yield as the sole product (Scheme 36) [258].

Hosokawa et al. [262] reported palladium(II)-catalyzed intramolecular processes for carbon–oxygen bond formation and developed the cyclization of 2-allylphenols to afford oxygen-containing heterocyclic compounds. However, the nature of palladium(II) salt affected the regioselectivity of the reaction to produce the five- or six-membered rings (Scheme 37). The six-membered products were formed predominantly in the presence of sodium salts of carboxylic acids containing electron-withdrawing substituents [263].

As compared to *o*-iodoanilines, *o*-iodophenols were utilized to produce the benzofurans in a one-pot protocol (Scheme 38). Cacchi and co-workers [264] utilized cuprous iodide and Pd(OAc)₂(PPh₃)₂ for the synthesis of variously substituted benzofurans from acetylenic derivatives and 2-iodophenols in 25–88% yield. This method was extended to the synthesis of furo[3,2-*b*]pyridines. This Pd catalyzed activation of alkynes toward nucleophilic attack was also adapted to oxygen nucleophiles to afford a pathway for the synthesis of benzofurans.

Scheme 36 Synthesis of tryptophan analogue

Cacchi [265] applied this in palladium acetate/cuprous iodide catalyzed Sonogashira coupling/cyclization of 2-halophenols with terminal alkynes. This approach has been expanded to the preparation of a variety of substituted benzofurans and related products, where the phenol unit was replaced with heterocyclic compounds, benzoquinone derivatives, and other polycyclic aromatic units [266–268].

The benzopyrone is present in various natural products such as flavonoids which interact with several receptor systems and enzymes of biological importance. Acyl chlorides derived from protected salicylic acids were utilized in Sonogashira coupling with terminal alkynes [269]. Benzopyrones were synthesized from alkynones by 6-*endo* cyclization under controlled conditions which preclude synthesis of aurones (Scheme 39).

The domino reaction for the synthesis of dihydroisobenzofuran was successfully transformed into a three-component reaction involving a one-pot coupling/

addition/cyclization sequence promoted by a base and Pd [270] (Scheme 40).

Different result was reported when 2-bromonicotinaldehyde was reacted with triethylsilylacetylene (TES). The main product was formed together with the desired desilylated compound in minor amounts. This was due to an early desilylation route occurring after the Sonogashira coupling, followed by a second coupling of terminal acetylene with 2-bromonicotinaldehyde, and a final addition/cyclization step (Scheme 41) [271–273].

The (*E*)-1,2-diiodoalkenes were reacted with terminal alkynes at room temperature in the presence of CuI and Pd(OAc)₂ to provide unsymmetrical buta-1,3-diyne selectively in moderate to good yields. The coupling of 2-ethynylphenol occurred with (*E*)-1,2-diiodoalkenes under same conditions, followed by a cyclization at 100 °C to afford ethynylbenzofurans [274] (Scheme 42).

The stoichiometric Pd reagents were utilized for several decades to assist this reaction, cyclization occurred

Scheme 37 Synthesis of 2,2-dimethyl-2*H*-chromene, 2-isopropylbenzofuran and 2-(prop-1-en-2-yl)benzofuran

Scheme 38 Synthesis of 2-phenylbenzofuran

Scheme 39 Synthesis of 2-methyl-4*H*-chromen-4-one and (*Z*)-2-ethylidene-3-oxo-2,3-dihydrobenzofuran-5-ylum

Scheme 40 Synthesis of dihydroisobenzofuran

Scheme 41 Synthesis of (Z)-2-((3-methoxyisobenzofuran-1(3H)-ylidene)methyl)benzaldehyde and 1-methoxy-3-methylene-1,3-dihydroisobenzofuran

Scheme 42 Synthesis of ethynylbenzofurans

Scheme 43 Synthesis of 2-ethylbenzofuran

with reduction to Pd(0), which was inactive for further reaction [275–277]. It was reported that the addition of stoichiometric oxidants like Cu(II) salts allowed the catalytic cyclization. For example, Hosokawa [278] observed that the catalytic cyclization of 2-allylphenols to benzofurans occurred upon the addition of copper acetate in the presence of oxygen and 2 mol% palladium acetate

(Scheme 43). This reaction occurred with good diversity and even at ambient temperature in water/DMF solvent.

Kundu et al. [279] reported the synthesis of Z-3-alkylidenephthalides as major products by Pd/Cu-catalyzed heteroannulation of o-iodobenzoic acids with terminal alkynes (Scheme 44). Phthalides were formed exclusively in many cases. The heteroannulation approach

Scheme 44 Synthesis of Z-3-alkylidenephthalides

was completely stereospecific, since only Z-isomers were formed.

2.12 Rhodium assisted synthesis

The ring systems were prepared, as shown by the total synthesis of (+)-elemen-8,12-olide, by intramolecular sulfur ylide formation and subsequent [2,3]-sigmatropic rearrangement (Scheme 45) [280–282]. The core structure was constructed from diazoketo esters in one step by rhodium acetate catalyzed reaction of intramolecular sulfonium ylide followed by [2,3]-sigmatropic rearrangement. The rearrangement occurred with high diastereoselectivity. Recently sulfonium ylide [2,3]-sigmatropic rearrangement was studied focusing on the development of new catalytic systems, including alternative carbene precursor other than commonly used diazocarbonyl compounds and new catalysts. Besides the most commonly used rhodium(II) and copper(I) catalysts, ruthenium [283, 284] and iron [285] complexes were utilized to catalyze the decomposition of diazo compounds to produce a metal carbene complex, which was trapped by allyl sulfide to induce [2,3]-sigmatropic rearrangement. For the carbene precursor, commercially available trimethylsilyldiazomethane was utilized which have some benefits over

the conventional diazocarbonyl compounds [286, 287]. A unique and interesting catalytic system, in which the rhodium(II) intermediate was produced by rhodium acetate catalyzed reaction of conjugated ene-yne-carbonyl compounds.

The conjugated ene-yne-carbonyl compounds underwent rhodium-mediated rearrangement for the synthesis of (2-furyl)carbenoids. The S-ylide formation occurred with subsequent 2,3-sigmatropic rearrangement in the presence of 10 equiv of an allyl sulfide, in analogy to the Doyle-Kirmse reaction of allyl sulfides with diazo compounds (Scheme 46) [288–291]. Good to excellent yields of coupling products were obtained, with an additional advantage that there was no need for slow addition of the carbene precursor. With diallyl sulfide, the reaction was performed at higher temperature to provide an access to subsequent Diels–Alder reaction with significant formation of complexity under mild reaction conditions. It was reported that the reaction of starting material with allylic sulfides occurred in catalytic amounts of rhodium acetate, and the furan possessing sulfides were formed in excellent yields [78–87, 111, 292].

The catalytic carbon-hydrogen insertion to metal carbenoids (derived from diazo compounds) occurred with chiral transition-metal catalysts in an enantioselective

Scheme 45 Synthesis of (3aR,5S,6S,7aR)-6-methyl-3-methylene-5-(prop-1-en-2-yl)-6-vinylhexahydrobenzofuran-2(3H)-one

manner. Davies and co-workers [293] reported that aryl-diazoacetates underwent asymmetric intramolecular reaction in the presence of $\text{Rh}_2(\text{S-DOSP})_4$ to afford the carbon-hydrogen insertion products (Scheme 47). The enantioselectivity strongly depends on the site of the carbon-hydrogen activation; the highest enantioselectivity was reported for insertion into the methyne carbon-hydrogen bond [78–87].

Similar to sulfur ylide synthesis, carbene transfer to phosphines, which sequentially underwent a Wittig type condensation with formyl groups, afforded phosphorus ylides. The catalytic reaction of carbonyl-ene-yne monomer bearing a formyl group was employed to the polycondensation reaction which provided π -conjugated polymers with low polydispersity (Scheme 48) [294–296]. The low polydispersity was maybe due to the low concentration of ylides but also to the selective reaction between the formed oligomeric ylides and a monomer substrate (carbonyl-ene-yne) involving a highly electrophilic formyl group para to a ketone functionality [111].

Stereoselective oxonium ylide reaction, especially asymmetric catalysis, has been a problem of considerable challenge in this field [297]. Since the first report of McKervy et al. [298] in the asymmetric induction of metal carbene-assisted ylide formation/[2,3]-sigmatropic rearrangement in 1992, efforts are being directed to this area. However, only limited success has been achieved so far. Following the initial use of dirhodium(II) tetrakis[(R)-binaphtholphosphate] $[\text{Rh}_2(\text{R-BNP})_4]$ where up to 30% enantiomeric excess was reported for the reaction of starting substrate, a variety of other chiral rhodium(II) catalysts [299–303] have been examined and up to 76% enantiomeric excess was obtained with Hashimoto's dirhodium(II) tetrakis[N-phthaloyl-(S)-tert-leucinate] $[\text{Rh}_2(\text{S-PTTL})_4]$ (Scheme 49) [287].

The enantio-enriched lactones [304, 305], chromanones [306], lactams [307], and cyclopentanones [308] were synthesized by asymmetric carbocyclizations on the basis of intramolecular carbon-hydrogen insertion of chiral rhodium carbenes. These reactions occurred with moderate

Scheme 46 Synthesis of (2-furyl)carbenoids

Scheme 47 Synthesis of (S)-methyl 2,2-dimethyl-2,3-dihydrobenzofuran-3-carboxylate

Scheme 48 Synthesis of (E)-1-(prop-1-enyl)-3-p-tolyl-4,5,6,7-tetrahydroisobenzofuran

to excellent enantioselectivity. Excellent enantio- as well as diastereoselectivity was achieved in the reactions of diazoacetates utilizing $\text{Rh}_2(4S\text{-MACIM})_4$ methyl 1-acetyl-2-oxoimidazolidine-4 α -carboxylate as a chiral catalyst, which afforded bicyclic lactones with 96–97% enantiomeric excess and 98% *de* [309] (Scheme 50).

Chung et al. [310] reported an intramolecular [5 + 2] and [4 + 2] cycloadditions in the presence of $[(\text{IPr})\text{Rh}(\text{COD})\text{Cl}]$ catalyst in conjunction with $\text{Ag}(\text{I})$ salt. This catalytic system was highly efficient for these two cyclizations, synthesizing, respectively, bicyclo[5.3.0]nonadiene and bicyclo[4.3.0]octadiene derivatives in high yields (Scheme 51). Despite the high activity reported for these intramolecular reactions, this system was not effective for intermolecular [5 + 2] cycloaddition [143].

The long-chain molecules were constructed, important in materials science, by [2 + 2 + 2] cycloaddition of alkynes.

McDonald et al. [311] reported the novel preparation of oligo-*p*-phenylenes, involving alkyne trimerization in the presence of rhodium catalyst as a key step (Scheme 52). Some phenylene products were useful in the construction of light-emitting and organic conducting polymers and were remarkably soluble in organic solvents. This type of multiple [2 + 2 + 2] cyclotrimerization reaction was a unique example so far [230, 312].

Witulski and co-workers [313] used Wilkinson's catalyst for the synthesis of chiral 3-substituted phthalides. Various α,ω -dialkynes were synthesized either through Mitsunobu coupling reactions or by standard dicyclohexylcarbodiimide (DCC) coupling reactions between the propargylic acid and propargyl alcohol derivatives. Chiral phthalide derivative was formed in good to excellent yields when dialkyne was treated with acetylene with the help of Wilkinson's catalyst (Scheme 53). The best results were reported when

Scheme 49 Synthesis of (*R*)-methyl 2-allyl-7-methyl-3-oxo-2,3-dihydrobenzofuran-2-carboxylate

Scheme 50 Synthesis of (3a*S*,7a*S*)-hexahydrobenzofuran-2(3*H*)-one

Scheme 51 Synthesis of bicyclo[5.3.0]nonadiene and bicyclo[4.3.0]octadiene derivatives

Scheme 52 Synthesis of oligo-*p*-phenylenes Scheme 53 Synthesis of 3-methyl-7-phenylisobenzofuran-1(3*H*)-one

the reactions were performed in the presence of 5 mol% of Wilkinson's catalyst and acetylene gas in toluene [312].

A model benzofuran unit of diazonium salt A was constructed by an intramolecular rhodium carbenoid aromatic carbon-hydrogen insertion reactions. The 2-bromophenol was easily transformed into diazoester (Scheme 54). The decomposition of diazoester was complex in the presence of rhodium(II) catalyst, and the benzofuranone was formed in only 20% yield. Subsequent C-acylation of benzofuranone for the preparation of oxazole ring was straightforward. The benzofuranone was obtained in 68% yield when ethyl chloroformate was reacted in the presence of 4-dimethylaminopyridine [314].

The viability of spirocyclopropene intermediate in the cycloaddition of dione to phenylacetylene in the presence of various chiral rhodium(II) complex catalysts, was reported by Muller [315], who rationalized that the lack of enantioinduction was an evidence for the intermediacy of compound.

Since both possible isomers of spirocyclopropene intermediate were *meso*-compounds, thermal rearrangement of the latter into furan synthesized a racemate, while the pathway via direct synthesis of rhodium(II)-carbenoid afforded enantiomerically enriched product. In contrast, previously it was reported that the rearrangement of achiral cyclopropenecarboxylates may also proceed enantioselectively in the presence of optically active rhodium(II) complexes [316]. Therefore, the absence of enantiomeric induction (Scheme 55) was not taken as unambiguous evidence for the involvement of cyclopropene intermediate and was simply a result of inefficacy of the chiral catalyst in this particular conversion [317, 318].

2.13 Samarium assisted synthesis

Armstrong and Du [319] reported a milder method for the preparation of solid-supported benzofurans via

Scheme 54 Synthesis of ethyl 7-bromo-2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-carboxylate

Scheme 55 Synthesis of 2,6-diphenyl-6,7-dihydrobenzofuran-4(5H)-one

Scheme 56 Synthesis of benzofurans

Scheme 57 Synthesis of 2-methyl-4,5,6,7-tetrahydrobenzofuran

samarium iodide assisted radical cyclization (Scheme 56) [320].

2.14 Silver assisted synthesis

Pale and co-workers [321] synthesized furans by a Brønsted acid and silver(I)-catalyzed rearrangement of epoxyalkyne. The reaction involved the opening of epoxide

with an alcohol in the presence of *p*-toluenesulfonic acid catalyst. The formed α -alkoxy- β -alkynols were reacted with Ag ions to provide a silver(I)-containing oxacyclic cation which provided furan derivatives finally (Scheme 57) [322].

The *o*-alkynylbenzoic acids were reacted for the synthesis of isocoumarins and/or alkylidenbenzofuranones in the presence of Ag catalyst (Scheme 58). The silver powder in dimethylformamide (warm) was proved to be the most

selective conditions which favored the 5-*exo*-dig cyclization. Bellina et al. [323] examined different catalysts for the cyclization of *o*-alkynylbenzoic acids; they found that silver nitrate favored the 6-*endo* approach (as Pd catalysts did) whereas silver promoted the synthesis of phthalides [324, 325].

Chiral dienes were synthesized efficiently by silver carbonate-catalyzed cyclization. The chiral dienes acted as key elements either for the synthesis of nagilactones or for a Diels–Alder approach to kaura-9(11)-16-dien-19-oic acid (Scheme 59) [324, 326, 327].

Intramolecular addition-cyclization reactions of ynone in the presence of Ag salts catalyst were reported in a few cases only. The aurones, a subclass of flavonoids, were prepared which contributed to the pigmentation of fruits and flowers and possess a number of pharmacological properties [328]. The 3-aryl-1-[2-hydroxyaryl]prop-2-yn-1-ones underwent 5-*exo*-dig cyclization for the synthesis of *Z*-aurones in catalytic amounts of AgNO₃ salt. When the phenol was intramolecular nucleophile, it was

possible to synthesize aurones (Scheme 60) via a high and efficient producing pathway, when starting compound was cyclized in the presence of silver nitrate in catalytic amounts. The isomeric flavones were formed in only traces [253, 324].

For alkenyl acids, the cyclization depends on the substitution and the chain length. This protocol offered one of the simplest procedures to produce lactones or cyclic ethers in good yields. This same reaction was also successfully employed to *o*-allylphenols. Here, Ag perchlorate in toluene was a better catalyst than Ag triflate [324, 329] (Scheme 61).

An intramolecular cyclization of phenol derivatives with a cadmium-carbon double bond on a side chain provided dihydrobenzofurans under the catalysis of Ag salts (Scheme 62). The nature of Ag-olefin complex affected the catalytic activity and was influenced by the distance between it and the Ag atom and the coordination ability of the counteranion [330]. Thus, a Ag cation bearing PF₆[−] or BF₄[−] as a counteranion, was strongly coordinated

Scheme 58 Synthesis of alkylidenebenzofuranones and/or isocoumarins

Scheme 59 Synthesis of (5*R*,7*aR*)-5-hydroxy-4,7*a*-dimethyl-3-methylene-5,6,7,7*a*-tetrahydroisobenzofuran-1(3*H*)-one

Scheme 60 Synthesis of (*Z*)-6-methyl-2-(4-methylbenzylidene)benzofuran-3(2*H*)-one

Scheme 61 Synthesis of 2-methyl-2,3-dihydrobenzofuran **Scheme 62** Synthesis of dihydrobenzofurans **Scheme 63** Synthesis of lactones or cyclic ethers **Scheme 64** Synthesis of *(Z)*-3-butyldiene-4,5-dihydroisobenzofuran-1(3*H*)-one and 3-propyl-5,6-dihydro-1*H*-isochromen-1-one

by cadmium–carbon double bond and oxygen atom of phenol derivatives and promoted no reaction. But the coordination of silver(I) by phenolic oxygen weakens the coordination ability of OTf^- and ClO_4^- and promoted the reaction efficiently [253].

Intramolecular additions of carboxyl or hydroxyl groups to inert olefins in the presence of Ag(I) triflate catalyst in 1,2-dichloroethylene was one of the newest and simplest protocols to synthesize lactones or cyclic ethers (Scheme 63) employing Ag-assisted chemistry [331]. The mechanism has proposed that the Ag(I) ion binds and activates the double bond to produce the complex, which was attacked by the oxygen-nucleophile on the opposite face. This provided an intermediate having newly formed C–O bond present *trans* to the Ag–C bond. Subsequently, proton transfer resulted in the regeneration of Ag(I) catalyst and the formation of product [253].

Many well stereodefined five-membered lactones were isolated from natural sources, and exhibit various pharmacological properties. Therefore, their preparation

has attracted the attention of chemists, and many organometallic protocols have been developed utilizing Ag and other metals [332]. For example, the natural product ligustilide was obtained in excellent stereo- and regioselectivities and good yield by the cyclization of alkynoic acid (Scheme 64) in the presence of catalytic amounts of silver or silver iodide [333]. A reaction sequence involving silver(I)-catalyzed lactonization of the alkyne as a key step provided lissoclinolide, an antibiotic butenolide, in a stereoselective manner [334]. The same protocol was applied for the synthesis of ligustilide starting from a structurally close alkyne [253, 335].

On the basis of substrate, the higher pyranone/furanone ratios were reported either with silver iodide, with silver in dimethylformamide and high dilutions [336, 337] or with silver carbonate in dimethylformamide (Scheme 65) [253, 338].

Marshall et al. [339–341] reported many examples of α -allenic alcohol stereospecific cyclizations. Cyclization of secondary alcohol was favored with α,α' -allenic diols,

Scheme 65 Synthesis of furanone and pyranone

Scheme 66 Synthesis of ((2*R*,7*aR*)-2-methyl-2,4,5,6,7,7a-hexahydrobenzofuran-2-yl) methanol Scheme 67 Synthesis of 2-chloro-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one Scheme 68 Synthesis of (*S*)-3-((*R*)-cyclohex-2-enyl)-3-methylisobenzofuran-1(3*H*)-one

possibly due to the preferential complexation of Ag^+ at the less congested end of the allenyl π -system [253] (Scheme 66).

The 1,3-dicarbonyl compound was oxidized with Ag(I) metal to produce the α -oxoalkyl radical which attacked the olefin to provide the radical. This nucleophilic adduct underwent oxidation with Ag(I) to afford a carbonium ion, which was cyclized to dihydrofuran. This strategy was employed for the total synthesis of the natural product α -clausenan [253, 342] (Scheme 67).

2.15 Zinc assisted synthesis

This reaction provided an excellent chemoselectivity when two active groups were involved. The allylic ZnCl_2 was reacted with 4-acetyl-benzoic acid methyl ester to afford the only single products in 95–96% yields. The 2-acetyl-benzoic acid methyl ester was treated with allylic ZnCl_2 to synthesize the lactone in an excellent diastereoselectivity as well as 97% yield (Scheme 68) [343].

Scheme 69 Synthesis of 2,5,6-trimethyl-3-phenylbenzofuran

Various benzofuran products with different structures were obtained by $\text{Zn}(\text{OTf})_2$ catalyzed cyclization of propargyl alcohols with phenols and anilines at 100 °C in toluene without additive. The oxazoles were formed by the cyclization of propargyl alcohols and amides [344] (Scheme 69).

3 Conclusion

The efficient and chemoselective synthesis of heterocycles by this technique has appeared as an important tool. This review shows a highly dynamic research field and the employment of metal and non-metal catalysts in organic synthesis. Several strategies have been pointed out in the past few years, to meet more sustainable, efficient and environmentally benign chemical products and procedures. The catalytic strategies have been focus of intense research because they avoid the use of toxic reagents. Among these catalytic strategies, highly rewarding and an important method in heterocycles synthesis is metal and non-metal catalyzed synthesis.

Funding There is no funding for this study.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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